



Metal-Organic Framework Glasses

Several Fundamental Problems - A plenary talk

Yue, Yuanzheng; Qiao, Ang; Bennett, Thomas D.; Tao, Haizheng; Greaves, Neville G.

Creative Commons License
Other

Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Yue, Y., Qiao, A., Bennett, T. D., Tao, H., & Greaves, N. G. (2017). *Metal-Organic Framework Glasses: Several Fundamental Problems - A plenary talk*. Abstract from The 9th China Symposium on Functional Glass and the International Forum on New Optoelectronic Materials, Fuzhou, China.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal -

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.

Metal-Organic Framework Glasses: Several Fundamental Problems

Yuanzheng Yue^{1,2}, Ang Qiao¹, Thomas D. Bennett³, Haizheng Tao¹, Neville G. Greaves^{1,3}

¹State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

²Department of Chemistry and Bioscience, Aalborg University, 9220 Aalborg, Denmark

³Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, CB2 3QZ, United Kingdom
yy@bio.aau.dk

Metal-organic frameworks (MOFs) are being extensively studied and developed owing to their potential applications such as gas absorption, catalysis, sensing, and so on. A subset of MOFs, called zeolitic imidazolate frameworks (ZIFs), has been found to be of particular interest due to their similar structure to that of zeolites. However, the melt-quenched ZIF glasses are of recent origin. It has been discovered that certain types of ZIFs can melt prior to decomposition, and hence, can be vitrified upon quenching.¹⁻³⁾ Study of this new category of glasses will provide new insights into general glass problems such as crystal-melting, glass formation, glass transition and relaxation. Compared to other categories of glasses (e.g., metallic, organic, and oxide glasses), ZIF glasses have been investigated to very limited extent. In this work, we present some initial advances in understanding the melting and glass formation of ZIFs, and enthalpy relaxation of ZIF glass. ZIF-4 ($\text{Zn}(\text{Im})_2$) and ZIF-62 ($\text{Zn}(\text{Im})_{1.75}(\text{bIm})_{0.25}$), where Im and bIm refer to imidazole and benzimidazole, respectively, are chosen as the objects of this study. Both ZIFs are different in many ways. ZIF-4 exhibits a striking polyamorphic transition, whereas ZIF-62 does not. Compared to ZIF-4 glass, ZIF-62 glass is far more stable against crystallization. The T_g/T_m ratio (0.84) of ZIF-62 has been found to be higher than that of any other glass-forming systems including ZIF-4, indicating that ZIF-62 is an extremely good glass former. The viscosity (10^5 Pa s) of ZIF-62 at T_m is significantly higher than that of most of glass-forming systems, but its fragility ($m=23$) is much lower. By analyzing the dynamic and structural data, we infer that the high steric hindrance and rigidity of the structure network are the origin of the ultrahigh glass forming ability of ZIF-62. We propose that the melting mechanism of glass-forming ZIF systems manifests as a combination of the Zn-N coordinating bond breaking-forming mode (described by Lindemann criterion) and the highly cooperative motion of structural units (metal-linker tetrahedra). From sub- T_g enthalpy relaxation study, we have found that a high degree of the structural heterogeneity is present in ZIF-62 glass.

1) T. D. Bennett, J. C. Tan, Y. Z. Yue, E. Baxter, C. Ducati, N. J. Terrill, H. H. M. Yeung, Z. Zhou, W. Chen, S. Henke, A. K. Cheetham, G. N. Greaves, *Nature Commun.* **6** (2015) 8079.

2) T. D. Bennett, Y. Z. Yue, P. Li, A. Qiao, H. Z. Tao, G. N. Greaves, T. Richards, G. I. Lampronti, S. A. T. Redfern, F. Blanc, O. K. Farha, J. T. Hupp, A. K. Cheetham and D. A. Keen, *J. Am. Chem. Soc.* **138** (2016) 3484.

3) H. Z. Tao, T. D. Bennett, Y. Z. Yue, *Adv. Mater.* **29** (2017) 1601705.